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PRESENT UNDERSTANDING OF THE VISCOELASTIC AND MECHANICAL PROPERTIES OF STEREOREGULAR POLYMERS

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INTRODUCTION

In the previous chapter a description of the behavior of the glass transition temperature (T_g) of vinyl and vinylidene polymers was presented and a theory (1) was put forward rationalizing the dependence of T_g on configuration in the case of vinylidene polymers. Here we review thermal, dynamic mechanical, and dielectric relaxation data for a series of poly(alkyl α chloroacrylates) of varying configurations (2,3,4). These data are further interpreted in the light of the theory mentioned above and the results compared with the corresponding poly(alkylmethacrylates).

In order to determine the effect of tacticity on properties it is necessary to prepare polymers of varied stereochemical structures ranging from the highly syndiotactic to the highly isotactic. Further, it is necessary to characterize the various stereoisomers both with regard to tacticity and to stereosequence distribution. These requirements have never been completely met. However, the poly(alkyl α chloroacrylates) studied in these laboratories probably represent as close an approximation to the requirements as has yet been attained. It was possible to synthesize stereoregular poly(α chloro methyl acrylates), poly(α chloro ethyl acrylates), and poly(α chloro isopropyl acrylates) (3), characterize them by NMR (5), and study their transition and relaxation behavior (4). Early work aimed at the synthesis of isotactic poly(alkyl α chloroacrylates) by the use of homogeneous anionic systems or Grignard reagent initiators invariably resulted in products with $\bar{M}_n < 10,000$ (6). In most instances these polymers would not form

films suitable for mechanical properties studies, and their T_g 's were low, necessitating a long extrapolation to obtain limiting values. It was only possible to obtain reasonably high molecular weight products by the use of a heterogeneous catalyst formed by the 1,4 addition reaction of a Grignard reagent to an unsaturated ketone (7).

EXPERIMENTAL

The preparation of the stereoregular poly(alkyl α chloroacrylates) used in this study has been described in detail previously (3). In summary, the highly syndiotactic polymers were obtained by a free radical, UV initiated polymerization at -50° or lower, the "conventional" polymers were obtained by free radical polymerization initiated by benzoyl peroxide at -70° , and the highly isotactic polymers were obtained by use of the Grignard reagent complex as initiator. The polymers were characterized primarily by the use of 300 MHz proton NMR (5). Relevant data for the samples used for property studies are collected in Table I.

Table I
Characterization Data For Stereoregular Poly(α Chloroacrylates)

Polymer	Fraction m Dyads(a)	$\bar{M}_n$ (b) (g/mole)
Poly(methyl α chloroacrylate)	0.70	80,000
"	0.29	270,000
"	0.25	400,000
Poly(ethyl α chloroacrylates)	0.73	309,000
"	0.29	362,000
"	0.20	181,000
Poly(isopropyl α chloroacrylates)	0.95	50,000
"	0.64	50,000
"	0.36	77,300

(a) From 300 MHz NMR (5)

(b) From membrane osmometry (3)

Films were prepared for mechanical and dielectric testing by casting 4% - 12% (w/v) solutions of the polymers in CHCl_3 on to clear plate glass and allowing the solvent to evaporate slowly. This procedure produced films of 4-8 mils thickness which were then dried in a vacuum oven at 60°C . for one to two days. After this treatment, it was found that the residual solvent, estimated to be less than 0.5% by weight by pyrolysis gas chromatography caused a decrease in T_g of up to 50°C . in the case of the syndiotactic poly(methyl α chloroacrylates) and about 25° to 30°C . in the case of the syndiotactic poly(ethyl α chloroacrylates) and poly(isopropyl α chloroacrylates). This residual solvent could not be removed by heating in a vacuum oven, and it

was found necessary to extract the films with methanol at ambient temperature for several days followed by a similar extraction with water. It is postulated that the large effect on T_g was due to some sort of complex formation between the polymer and the CHCl_3 . Further studies are necessary to elucidate the nature of this complex.

The mechanical measurements were carried out on a Rheovibron Dynamic Viscoelastometer, Model DDVII. The frequencies employed were 3.5 Hz, 11 Hz, and 110 Hz, and the temperature range was from -100°C . to $+170^\circ\text{C}$. depending on the T_g of the polymer under observation. $\tan \delta$, E' and E'' were obtained at the quoted frequencies as functions of temperature by standard techniques.

Dielectric measurements were carried out with a General Radio capacitance bridge, type 1620-A, in conjunction with a Balabaugh Lab. three terminal cell, type LD-3. The dielectric loss tangent and the real and imaginary parts of the dielectric constant, ϵ' and ϵ'' were obtained as functions of temperature at 6 frequencies: 200 Hz, 500 Hz, 1 kHz, 2 kHz, 5 kHz, and 10 kHz. The temperature range investigated was from room temperature to $+190^\circ\text{C}$.

Differential Scanning Calorimetry (DSC) measurements were carried out using a Perkin Elmer instrument, model DSC-1B. The scanning rate was $20^\circ\text{C}/\text{minute}$ in all cases and calibrations for determining heats of fusion were accomplished using naphthalene, adipic acid, or benzoic acid for the appropriate temperature ranges.

RESULTS AND DISCUSSION

Figure 1 presents the dyad tacticity determined from 300 MHz NMR (5) versus the T_g measured by DSC for the poly(alkyl α chloroacrylates) studied. All values are corrected to "infinite" molecular weight as follows. The molecular weight dependence of T_g for a linear polymer is given by the Flory-Fox relationship

$$T_g = T_{g\infty} - K/\bar{M}_n \quad (1)$$

where T_g is the observed value for a polymer of a given molecular weight and $T_{g\infty}$ is the limiting value. The constant, K , is typically in the range of 10^5 for poly(styrene), poly(methyl methacrylate), and many other non-polar polymers. Thus for $\bar{M}_n > 10^5$, the T_g 's of such polymers are essentially independent of molecular weight. In the case of stereoregular poly(methyl methacrylates), it has been stated that K depends on tacticity, varying from about 1.0×10^5 for 100% isotactic dyads, to 4.0×10^5 for 100% syndiotactic dyads (8). The results of the

Dependence of Glass Transition
Temperatures (DSC) of Poly(Alkyl
 α -Chloroacrylates) on Tacticity
(300 MHz NMR).

Figure 1

simultaneous solution of eq. (1) for various molecular weight stereoregular poly(alkyl α chloroacrylates) gave $K = 1.0 \times 10^5$ for the highly isotactic polymers and $K = 3.0 \times 10^5$ for the highly syndiotactic polymers (3). These values were then used to determine the T_g 's which are plotted in Figure 1. The observed dyad tacticity dependences of T_g are good straight lines in all cases making it possible to extrapolate the observed values to the 100% syndiotactic case on the one hand and to the 100% isotactic case on the other. Despite the apparently straightforward extrapolations displayed in Figure 1, the procedure may be criticized on several grounds. First, the highly isotactic poly(alkyl α chloroacrylates) prepared by the use of the modified Grignard reagent catalyst are extremely blocky, while the "conventional" and highly syndiotactic polymers prepared by free radical initiators are all more or less random (5). It is well known that sequence distributions can have a large effect on T_g . Thus the type of relationships implied by Figure 1 are really only valid for a series of polymers in which the configuration varies but the sequence distribution remains the same. Second, Bywater and Toporowski (9) have shown that in the case of the stereoregular poly(methylmethacrylates), T_g approaches an asymptotically limiting value of 120° at high degrees of syndiotacticity. Previously, the assumption of a straight line relationship between T_g and configuration in poly(methylmethacrylate) resulted in an extrapolated value for the 100% syndiotactic polymer of 160° (8). It is therefore apparent that the T_g values for 100% isotactic and syndiotactic poly(alkyl α chloroacrylates) obtained from Figure 1 must be only provisionally accepted pending further elucidation of stereosequence effects and behavior at

high degrees of syndiotacticity.

T_m's are also observable by DSC for the most highly isotactic poly(alkyl α chloroacrylates), and an intermediate transition labelled T_i is observable for isotactic poly(methyl α chloroacrylates) at 159°C. These data are summarized in Table II.

As discussed in detail in the previous chapter, the T_g difference between any pair of stereoisomers is given by

$$T_g(\text{syndiotactic}) - T_g(\text{isotactic}) = 0.59 \Delta\epsilon/k \quad (2)$$

where T_g(syndiotactic) is the glass transition temperature of the syndiotactic isomer, T_g(isotactic) is the glass transition temperature of the isotactic isomer, Δε is the difference in the flex energy between the syndiotactic isomer and the isotactic, and k is Boltzmann's constant. It was originally deduced that, for the methacrylates,

$$T_g(\text{syndiotactic}) - T_g(\text{isotactic}) = 112^\circ \quad (3)$$

Subsequently the relationship was applied to stereoregular poly(ethyl α chloroacrylates) (2) and was found to be

$$T_g(\text{syndiotactic}) - T_g(\text{isotactic}) = 90^\circ \quad (4)$$

In the present work, the values obtained are based on more complete NMR analyses of tacticity at higher frequencies and a much greater range of stereoregular isomers. These results are for the methyl ester

$$T_g(\text{syndiotactic}) - T_g(\text{isotactic}) = 92^\circ \quad (5)$$

for the ethyl ester

$$T_g(\text{syndiotactic}) - T_g(\text{isotactic}) = 80^\circ \quad (6)$$

for the isopropyl ester

$$T_g(\text{syndiotactic}) - T_g(\text{isotactic}) = 68^\circ \quad (7)$$

The T_g differences decrease with increasing ester side chain length or bulkiness in contradiction to the simple theory. Also, the values are all considerably smaller than that originally quoted for the stereoregular poly(methylmethacrylates). The value quoted in eq. (3) was based on an extrapolated T_g for the 100% syndiotactic poly(methylmethacrylate) of 160°. If Bywater's value of 120°, (discussed above), is accepted we obtain an amended figure of 80° for the T_g difference between the stereoisomers of poly(methyl methacrylate). In view of the uncertain-

Table II
Thermal Transitions of Stereoregular Poly(alkyl α chloroacrylates)

<u>Polymer</u>	<u>Tacticity (m dyads)^(a)</u>	<u>T_g^(b) (°C.)</u>	<u>T_s (°C.)</u>	<u>T_m (°C.)</u>
Poly(methyl α chloroacrylate)	0.70	90	152	186
" "	0.29	152	--	--
Poly(ethyl α chloroacrylate)	0.73	52	--	109
" "	0.20	104	--	--
Poly(isopropyl α chloroacrylate)	0.95	70	--	191
" "	0.36	110	--	--

(a) Derived from 300 MHz NMR (5)

(b) Corrected to "infinite" molecular weight (3)

ties in the extrapolation procedure, the difference between the methyl esters, eq. (5) and the ethyl esters, eq. (6) are probably not significant. However, the value for the isopropyl esters, eq. (7), is certainly lower. The theory embodied in eq. (2) rests on the validity of the Gibbs-DiMarzio approach to the glass transition. In addition it is assumed that T_g is an iso-free volume state and that inter- and intra-molecular effects on T_g are strictly separable. The experimental disagreement with the theory for the case of the isopropyl esters is probably mainly due to the breakdown of this latter assumption. That is, the isopropyl ester side group has a significant effect on the energetics of chain conformations as well as affecting the free volume. In spite of these considerations, it is clear that the simple theory does remarkably well in rationalizing configurational effects on the T_g 's of both poly(alkyl methacrylates) and poly(alkyl α chloroacrylates). Its predictive value is certainly limited inasmuch as $\Delta\epsilon$ cannot at present be calculated from a knowledge of molecular structure.

Turning to the crystallization behavior, it is perhaps surprising that any crystallization occurs at all in the isotactic poly(methyl α chloroacrylates) and poly(ethyl α chloroacrylates) which have only about 0.7 fractions of *m* dyads. The effect, however, is traceable to the blocky nature of those polymers prepared using the modified Grignard reagent catalyst and to the fact that there is considerable stereo inhomogeneity in these polymers as demonstrated by fractionation which results in portions of greatly enhanced stereoregularity (3). It should be pointed out that the observed enthalpies of fusion are small, of the order of 2 cal/g for both the methyl and ethyl polymers and of the order of 8 cal/g for the more highly isotactic isopropyl polymer. The enthalpies of fusion for the 100% crystalline poly(alkyl α chloroacrylates) are unknown, but if the reported value for isotactic poly(methylmethacrylate) of 22 cal/g (10) is used as a rough basis of comparison, it is apparent that the degrees of crystallinity are low.

A quantitative assessment of the weight fraction crystallinity is not possible in the absence of information about the theoretical enthalpies of fusion and the size of the crystals. The appropriate relationships are:

$$W_c = \frac{\Delta H_{\text{observed}}}{\Delta H_{\text{theoretical}}(\infty)} \quad (8)$$

where W_c is the weight fraction crystallinity, $\Delta H_{\text{observed}}$ is the experimental enthalpy of fusion and $\Delta H_{\text{theoretical}}(\infty)$ is the enthalpy of fusion for the hypothetical 100% crystalline polymer. $\Delta H_{\text{theoretical}}$ is obtained on the basis of several well established extrapolation procedures (11). Eq. (8) applies

to the case where the crystal is "infinitely" thick. For these crystals, ΔH theoretical must be modified as follows

$$\Delta H_{\text{theoretical}} = \Delta H_{\text{theoretical}}(\infty) - 2\Delta H_e/l \quad (9)$$

where $\Delta H_{\text{theoretical}}(\infty)$ refers to the "infinitely" thick perfect

crystal, ΔH_e is the excess enthalpy associated with forming the basal surfaces of the lamellar crystal and l is the crystal thickness. Even if the $\Delta H_{\text{theoretical}}(\infty)$ were known for the poly

(alkyl α chloroacrylates), it is probable that the correction factor, $\Delta H_e/l$, would be of considerable importance, since the rather low degrees of stereoregularity would favor the formation of small crystals. Wide angle x-ray diffraction patterns of the unoriented materials reveal a very low degree of crystalline order, although it has been possible to obtain lattice parameters from such measurements on specimens oriented above their T_g 's (3). A frequently quoted empirical observation is that the ratio (T_g/T_m) lies in the range of 0.50 to 0.75 for many polymers. If we evaluate this ratio for the isotactic poly(alkyl α chloroacrylates) studied we find values of 0.79, 0.85 and 0.74 for the methyl, ethyl, and isopropyl polymers respectively. Using literature values for isotactic poly(methylmethacrylate), a value of 0.74 is obtained (12). Thus, only poly(isopropyl α chloroacrylate) behaves in a "normal" fashion. It is well known that many exceptions to the empirical generalization exist (13). In the present case, the probable presence of small crystals would indicate depressed melting points as well as low enthalpies of fusion and this might account for the high ratios for the methyl and ethyl polymers.

The presence of a third transition between the T_g and T_m in the case of the isotactic poly(methyl α chloroacrylate) has been commented on previously and evidence has been presented for the assignment of this phenomenon to the glass transition of a stereocomplex of isotactic and syndiotactic polymer molecules (3). It is not possible to confirm or reject this hypothesis on the basis of available evidence.

The results of the mechanical and dielectric relaxation studies are embodied in Table III and Figs. (2), (3), and (4). An inspection of Figs. 2-4 reveals that all of the polymers show a prominent relaxation associated with the glass transition and labelled α in Table II. As expected, the temperatures and activation energies of these relaxations are strong functions of the steric structures of the polymers. The activation energies listed in Table III are obtained from the slopes of plots of the logarithm of the maximum frequency of the dielectric loss

TABLE III
Activation Energies of Relaxation Processes in Poly(alkyl α chloroacrylates)

<u>Polymer</u>	<u>m Dyads</u>	<u>Temp. Range For Dielectric (D) & Mechanical (M) Loss Maxima ($^{\circ}$C.)</u>	<u>Activation Energy^a k cal/mole</u>	<u>Relaxation Process</u>
Poly(methyl α chloroacrylate)	0.70	117-127 (D)	120 $\pm$ 5	α
"	" "	103-111 (M)		
"	" "	~180 (D)		α_{sc}
"	" "	~160 (M)		
"	0.29	169-174 (D)	150 $\pm$ 9	α
"	" "	154-161 (M)		
"	" "	120-150 (D)		β
"	"	100-110 (M)		
"	0.25	176-185 (D)	154 $\pm$ 16	α
"	"	161-166 (M)		
"	"	125-160 (D)	38 $\pm$ 4	β
"	"	100-110 (M)		
Poly(ethyl α chloroacrylate)	0.73	92-119 (D)	44 $\pm$ 1	α
"	"	68-74 (M)		
"	0.29	126-142 (D)	85 $\pm$ 5	α
"	"	101-111 (M)		
"	0.29	~70 (M)		β

(cont'd.)

TABLE III (cont'd.)

<u>Polymer</u>	<u>m Dyads</u>	<u>Temp. Range</u>	<u>Activation</u> <u>Energy^a</u> <u>k cal/mole</u>	<u>Relaxation</u> <u>Process</u>
		<u>For Dielectric (D)</u> <u>& Mechanical (M)</u> <u>Loss Maxima (°C.)</u>		
Poly(ethyl α chloroacrylate)	0.20	132-146 (D)	99 $\pm$ 5	α
		109-117 (M)		
		~70 (M)		
Poly(isopropyl α chloroacrylate)	0.36	128-148 (D)	63 $\pm$ 3	α
		106-117 (M)		

(a) From Dielectric Data only.

Figure 2: Upper temperature dependence of E' and E'' , at 200 Hz for (A) isotactic poly(methyl α -chloroacrylate), (B) atactic poly(methyl α -chloroacrylate), and (C) syndiotactic poly(methyl α -chloroacrylate). Lower: temperature dependence of the dielectric constant and loss at 200 Hz for (A) isotactic poly(methyl α -chloroacrylate), (B) atactic poly(methyl α -chloroacrylate), and (C) syndiotactic poly(methyl α -chloroacrylate).

Figure 3: Upper temperature dependence of E' and E'' at 200 Hz for (A) isotactic poly(ethyl α -chloroacrylate), (B) atactic poly(ethyl α -chloroacrylate), and (C) syndiotactic poly(ethyl α -chloroacrylate). Lower: temperature dependence of the dielectric constant and loss at 200 Hz for (A) isotactic poly(ethyl α -chloroacrylate), (B) atactic poly(ethyl α -chloroacrylate), and (C) syndiotactic poly(ethyl α -chloroacrylate).

Figure 4: Left: temperature dependence of E' and E'' at 200 Hz for syndiotactic poly(isopropyl α -chloroacrylate). Right: temperature dependence of the dielectric constant and loss at 200 Hz for syndiotactic poly(isopropyl α -chloroacrylate).

constant ($\log f_{\max}$) versus $1/T$. Inasmuch as only 3 frequencies are available mechanically (3.5, 11 and 110 Hz), it is difficult to derive reliable values from the mechanical results. It can be said, however, that the dielectric and mechanical α relaxations correlate well with one another and are consequences of the same molecular motions (i.e., microbrownian segmental motions accompanying T_g).

Activation energies for relaxation phenomena associated with the glass transition are commonly interpreted according to the WLF formalism (14)

$$\log a_T = \frac{C_1(T - T_g)}{C_2 + T - T_g} \quad (10)$$

where a_T is the "shift factor", and C_1 and C_2 are "universal" constants for all amorphous polymers.

a_T may be written as the ratio of the relaxation time at temperature T to that at T_g . If we further interpret the frequency of maximum loss in either the mechanical or dielectric relaxation curves as being equal to the reciprocal of the relaxation time a plot of the logarithm of the maximum loss frequency versus reciprocal temperature will yield a temperature dependent activation energy according to eq. (10) as follows

$$E_a = (2.303 C_1 C_2 R T^2) / (C_2 + T - T_g)^2 \quad (11)$$

At T_g , eq. (10) reduces to

$$E_a = 2.303(C_1/C_2)R T_g^2 \quad (12)$$

In eqn's. (11) and (12) E_a is the activation energy and R is the gas constant. The preceding analysis is only approximate because it is based on a number of assumptions which are more or less unrealistic. It is beyond the scope of this treatment to discuss these points in detail, but standard treatises such as that of Ferry (15) may be consulted. Although the actual plots of $\log f_{\max}$ vs $1/T$ from which the data in Table III are derived are not shown, they were all straight lines over the frequency and temperature range studied. This is because of the limited ranges available. Presumably, if a greater frequency and temperature range had been examined the plots would have exhibited curvature in at least qualitative accord with eq. (11). It may be further noted, that according to eq. (12), the activation energies for the α relaxation process at T_g should be in the ratio

$$E_a(\text{syndio})/E_a(\text{iso}) = [T_g(\text{syndio})/T_g(\text{iso})]^2 \quad (13)$$

In eq. (12) $E_a(\text{syndio})$ is the activation energy for the α process in the syndiotactic isomer and $E_a(\text{iso})$ is the corresponding activation energy for the isotactic isomer. The T_g values refer to the calorimetric T_g 's for the appropriate stereoisomers. A comparison of the observed activation energy ratio with those calculated from eq. (13) for the various esters yields, for the methyl esters

$$\begin{aligned} (E_a \text{ syndio}/E_a \text{ iso}) \text{ observed} &= 1.3 \\ (E_a \text{ syndio}/E_a \text{ iso}) \text{ calculated} &= 1.2 \end{aligned} \quad (14)$$

For the ethyl esters

$$\begin{aligned} (E_a \text{ syndio}/E_a \text{ iso}) \text{ observed} &= 2.3 \\ (E_a \text{ syndio}/E_a \text{ iso}) \text{ calculated} &= 1.4 \end{aligned} \quad (15)$$

In view of the experimental uncertainties and the approximations inherent in the analysis, it is apparent that the simple treatment embodied in eqn's. (10)-(13) accounts for the observed activation energy trends in the stereoisomers studied.

A secondary relaxation occurring in the glassy state had previously been reported for "conventional" poly(methyl α chloroacrylates) prepared by free radical techniques (16). This β relaxation occurs also in the poly(alkylmethacrylates) and is assigned to motions of the ester side group about the carbon-carbon bond joining it to the main chain. It is discernible

only in the highly syndiotactic methyl and ethyl polymers and is absent in the syndiotactic isopropyl polymers. It is a minor feature throughout and is not observable dielectrically for the syndiotactic ethyl polymer. The dielectric behavior of the β relaxation in the poly(alkyl α chloroacrylates) is in marked contrast to its behavior in the poly(alkylmethacrylates). In the latter case, "conventional" or syndiotactic poly(methylmethacrylate) has a dielectric β relaxation considerably greater in magnitude than the α relaxation in the same polymer, while the situation is reversed in isotactic poly(methylmethacrylate) (17). This observation is interpretable on the basis that the side chain relaxation occurs independently of the main chain relaxation in the syndiotactic poly(methylmethacrylates) but is correlated with the main chain relaxation in the isotactic poly(methylmethacrylates). The greater dipole moment of the ester side chain compared to the α methyl group then accounts for the observed dielectric relaxation magnitudes. In the poly(alkyl α chloroacrylates), the polar α Cl group introduces a main chain dipole moment of much greater magnitude than that of the ester side chain, and so the α relaxation is the predominant dielectric feature regardless of the tacticity of the polymer. The absence of the β relaxation in the isotactic poly(alkyl α chloroacrylates) does suggest that the ester side chain motion may merge with that of the main chain in these polymers in a similar manner to what is postulated to occur in the isotactic poly(methylmethacrylates).

The relaxation labelled α_{SC} for the isotactic poly(methyl α chloroacrylate) in Table II is thought to correlate with the transition observed by DSC at 150° and is tentatively assigned to motions accompanying the glass transition of the "stereocomplex" postulated to occur in these polymers, composed of isotactic and syndiotactic chains.

The only previous report of activation energies for poly(methyl α chloroacrylates) is for the "conventional" free radical polymer which can be assumed to be reasonably syndiotactic (16). The values quoted are 130 kcal/mole for the α relaxation and 26 kcal/mole for the β relaxation. The present results (Table II) are in qualitative agreement with these values. In general the activation energies for the α relaxations decrease with increasing ester side chain length or bulkiness and the isotactic isomers have α relaxation activation energies about 35-50 kcal/mole lower than the comparable syndiotactic isomers. This effect, as already discussed, is a consequence of the T_g difference between the isomers.

CONCLUSIONS

(1) The Tg's of stereoregular poly(alkyl α chloroacrylates) are strong functions of tacticity and can be rationalized, to a first approximation, on the basis of the previously proposed theory.

(2) Evidence exists for the presence of a stereocomplex composed of a combination of isotactic and syndiotactic poly(methyl α chloroacrylate).

(3) Crystallinity can be observed for the highly isotactic poly(alkyl α chloroacrylates).

(4) The relaxation behavior accompanying the glass transitions (α relaxation) in stereoregular poly(alkyl α chloroacrylates) is generally in accord with previous results on atactic polymers. The activation energies for the α relaxation process in the various stereoisomers can be accounted for on the basis of the WLF treatment.

(5) The secondary or β relaxation, assigned to motions of the ester side group is a minor feature dielectrically in contrast to the behavior of the poly(alkylmethacrylates).

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